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AUTOXIDATION OF POLY(ALKYLENE GLYCOLS) IN SOLUTION

by

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and

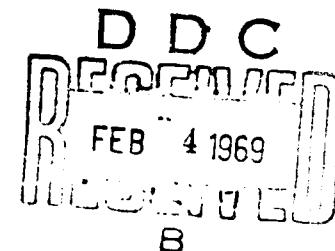
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SUMMARY

Data reported for the autoxidation of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) in solution at relatively long reaction times were analyzed. A relatively simple and a more general kinetic scheme with corresponding rate expressions were used. It was found that the more general scheme gave somewhat more satisfactory agreement between calculated and observed values of several reaction variables. Limitations in the applications of both schemes to PEG and PPG autoxidations are mentioned.

Introduction

A general kinetic scheme for the uncatalyzed, uninhibited autoxidation of polypropylene in the bulk phase was first reported by Stivala, Reich, and co-workers¹ in 1963. Since then they have reported on various kinetic aspects of the autoxidation of polyolefins in the bulk phase using this general scheme. Thus, rates of: carbonyl and hydroperoxide formation,²⁻⁵ oxygen absorption,^{6,7} and volatile products^{3,5} formation were investigated along with chemiluminescence,^{5,6} changes in intrinsic viscosity as a function of time,^{8,9} and autoxidation in the presence of inhibitors.¹⁰ Recently, Bawn and Chaudhri^{11,12} successfully extended the general scheme presented by Reich, Stivala, and co-workers to the autoxidation of polypropylene in solution (at relatively high polymer concentrations). At relatively low polymer concentrations, a much simpler scheme was found to be valid in which termination of polymeric peroxy radicals by recombination was postulated¹³ (which the general scheme mentioned earlier did not include).

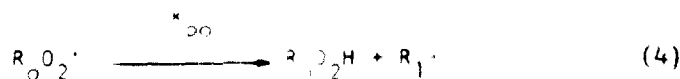
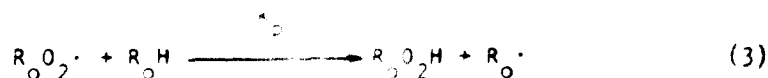
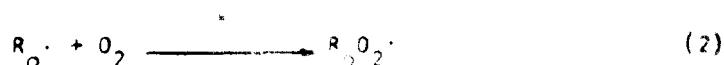
Recently, Grosborne and coworkers¹⁴ reported on a kinetic study of the autoxidation of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) in solution in the presence of the free radical initiator azodicyclohexane-nitrile (ADCN). These investigators developed kinetic expressions which could satisfactorily explain various aspects of the autoxidation of PEG and PPG during initial reaction conditions (at very low conversions). They assumed that termination of polymeric peroxy radicals by recombination occurred along with intra- and intermolecular propagation. However, these workers did not analyze their data for the autoxidation of PEG and PPG as a function of reaction time (for relatively high conversions).

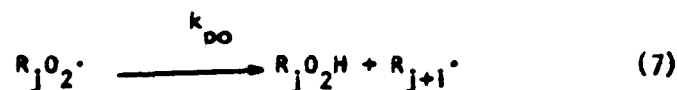
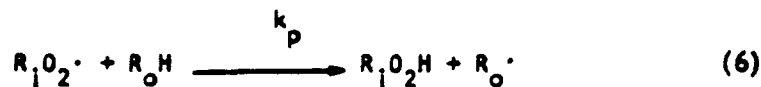
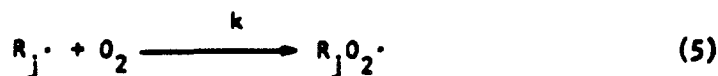
It is the purpose of this paper to present an analysis of the data obtained by Grosborne and coworkers¹⁴ for the autoxidation of PEG and PPG as a function of reaction time. We will utilize basic ideas previously presented in our general scheme¹⁻¹⁰ for the formation of carbonyl moieties and of hydroperoxide, and for changes in intrinsic viscosity as a function of reaction time. Two schemes will be employed in our analysis. Both will involve free radical processes; however, a major difference is that one involves termination of polymeric peroxy radicals by recombination (simple scheme) whereas the other does not (general scheme).

II. Theory

A. Scheme with termination of polymeric peroxy radicals by recombination

During the initial stages for the autoxidation of PEG and PPG in solution, the following scheme was assumed to apply,¹⁴





where, k_{po} and k_p denote the rate constants for intra- and intermolecular propagation, respectively; and, R_oH represents the unoxidized substrate.

For relatively long kinetic chain lengths and from steps (1) - (8), the following rate of oxidation (ρ_{ox}) expression may be obtained,¹⁴

$$\rho_{ox} = R_p + (R_i + R_p) \sum_{j=1}^n \left(\frac{k_{po}}{D} \right)^j \quad (9)$$

where, $R_p = k_p [R_oH] R_i^{1/2} k_t^{-1/2}$, R_i denotes the rate of radical initiation from ADCN; $D = k_{po} + k_p [R_oH] + (k_t R_i)^{1/2}$; and, n denotes the number of successive intramolecular propagations.

At relatively high conversions, Eq. (9) should no longer be valid, and the following additional initiation step must be considered,



Thus, at long reaction times, it would be anticipated that the concentration of hydroperoxide would attain a relatively high limiting value.^{15,16} Since

the rate constant for polypropylene hydroperoxide decomposition^{7,17} is about thirty times that for ADCN decomposition at 95°C, it would be expected that as the autoxidation proceeds and the PEG and PPG hydroperoxide concentration rises, initiation via hydroperoxide decomposition (R'_i) would predominate over initiation via ADCN decomposition (R_i).

1. Rate of hydroperoxide formation

From the preceding, we may write for the initiation rate after initial oxidation stages,

$$R'_i = 2 k_i \sum [R_j O_2 H] \quad (10)$$

Furthermore, it is assumed that intramolecular propagation is inoperative during the autoxidation at relatively high reaction times. Due to chain scission during the autoxidation, the number of hydrogens per polymer molecule which would be available for intramolecular propagation would be greatly diminished (also, the inclusion of intramolecular propagation resulted in kinetic expressions which gave calculated values of variables which disagreed more with observed values than when intramolecular propagation was neglected). Thus, we may also write,

$$\frac{d(\sum [R_j O_2 H])}{dt} \equiv \rho_{HP} = k_p [RH] \sum [R_j O_2 \cdot] - \frac{R'_i}{2} \quad (11)$$

or,

$$\rho_{HP} = \frac{k_p [RH] (k_i \sum [R_j O_2 H])^{1/2}}{k_t^{1/2}} - k_i \sum [R_j O_2 H] \quad (12)$$

Assuming that k_p , k_t , and $[RH]$ are approximately constant during the PEG autoxidation, Eq. (12) may be integrated to give,

$$\ln \left(1 - \frac{k_i}{B} [HP]^{1/2} \right) = - \frac{k_i}{2} t \quad (13)$$

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where, $B = k_i^{1/2} k_t^{-1/2} k_p [RH]$; and, $[HP] = \sum [R_j O_2 H]$. At relatively long reaction times, $B/k_i = [HP]_{\infty}^{1/2}$, and Eq. (13) becomes,

$$\ln \left[1 - \left(\frac{[HP]}{[HP]_{\infty}} \right)^{1/2} \right] = - \frac{k_i}{2} t \quad (14)$$

Upon differentiating, Eq. (14) becomes,

$$\ln \frac{\rho_{HP}}{[HP]^{1/2}} = \ln B - \frac{k_i}{2} t \quad (15)$$

Expressions will now be derived from the preceding equations for rates of autoxidation (ρ_{ox}) and ester formation (ρ_{co}), and for changes in intrinsic viscosity as a function of reaction time.

2. Rate of Autoxidation

$$\rho_{ox} = k[O_2] \sum [R_j \cdot] - R_i/2 \quad (16)$$

and,

$$\rho_{ox} = k_i [HP] + \frac{k_p [RH] (k_i [HP])^{1/2}}{k_t^{1/2}} \quad (17)$$

Upon substituting the expression for $[HP]$ from Eq. (14) into Eq. (17) and integrating,

$$\begin{aligned} \Delta[O_2] = & 2 k_i [HP]_{\infty} t + 6 [HP]_{\infty} \left(e^{-\frac{k_i}{2} t} - 1 \right) \\ & - [HP]_{\infty} \left(e^{-k_i t} - 1 \right) \end{aligned} \quad (18)$$

3. Rate of Ester Formation

From previously reported work,²⁻⁵

$$\rho_{CO} = f k_i [HP] \quad (19)$$

where, f denotes a proportionality factor. Upon combining Eqs. (14) and (19), the following expressions can be derived,

$$\Delta([> c=O]) = (\rho_{CO})_{\infty} t + 4 \frac{(\rho_{CO})_{\infty}}{k_i} \left(e^{-\frac{k_i}{2}t} - 1 \right) - \frac{(\rho_{CO})_{\infty}}{k_i} \left(e^{-k_i t} - 1 \right) \quad (20)$$

and,
$$\ln \left[1 - \left(\frac{\rho_{CO}}{(\rho_{CO})_{\infty}} \right)^{1/2} \right] = -\frac{k_i}{2} t, \quad (20')$$

where, $(\rho_{CO})_{\infty} = f k_i [HP]_{\infty}$.

4. Intrinsic Viscosity Changes

Based upon previously reported work,^{8,9} let

$$\Delta\eta = \left(\frac{[\eta]}{[\eta]_0} \right)^{1/a} - 1 = f_1 [> c=O] \quad (21)$$

where, f_1 = proportionality factor; $[\eta]_0$ and $[\eta]$ denote intrinsic viscosities which PEG possesses initially and during autoxidation, respectively; and,

a = Mark-Houwink exponent (0.77 for PEG). Substituting the expression for $[> c=O]$ from Eq. (20) into Eq. (21),

$$\Delta\eta = f_1 (\rho_{CO})_{\infty} t + 4 f_1 \frac{(\rho_{CO})_{\infty}}{k_i} \left(e^{-\frac{k_i}{2}t} - 1 \right) - \frac{f_1 (\rho_{CO})_{\infty}}{k_i} \left(e^{-k_i t} - 1 \right) \quad (22)$$

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8. Scheme without termination of polymeric peroxy radicals by recombination

The general scheme and the corresponding equations derived therefrom¹⁻¹⁰ were utilized to obtain expressions for various variables in the autoxidation of PEG and PPG.

1. Rate of hydrperoxide formation

From the general scheme previously referred to, it can readily be shown that,

$$[HP] \approx [HP]_{\infty} (1 - e^{-At}) \quad (23)$$

or,
$$\ln \left(1 - \frac{[HP]}{[HP]_{\infty}} \right) = -At \quad (23a)$$

Upon differentiating, Eq. (23), becomes,

$$\rho_{HP} = A[HP]_{\infty} e^{-At} \quad (24)$$

or
$$\ln \rho_{HP} = \ln(A[HP]_{\infty}) - At \quad (24a)$$

2. Rate of ester formation

It can be shown¹⁻¹⁰ that

$$\rho_{CO} = (\rho_{CO})'_{\infty} \left(1 - e^{-At} \right) \quad (25)$$

where, $(\rho_{CO})'_{\infty} = k_6[HP]_{\infty}$. Equation (25) may be rearranged to give,

$$\ln \left(1 - \frac{\rho_{CO}}{(\rho_{CO})'_{\infty}} \right) = -At \quad (25a)$$

Furthermore, from Eq. (25),

$$\Delta([>C=O]) = (\rho_{CO})'_\infty t + \frac{(\rho_{CO})'_\infty}{A} (e^{-At} - 1) \quad (26)$$

3. Rate of autoxidation

$$\rho_{ox} = R_i + k_5[HP] \quad (27)$$

and,

$$\rho_{ox} = R_i + k_5[HP]_\infty (1 - e^{-At}) \quad (28)$$

From Eq. (28),

$$\Delta[O_2] = R_i t + k_5[HP]_\infty t + \frac{k_5[HP]_\infty}{A} (e^{-At} - 1) \quad (29)$$

4. Intrinsic viscosity changes

Upon substituting Eq. (26) into Eq. (21),

$$\Delta\eta = f_1(\rho_{CO})'_\infty t + \frac{f_1(\rho_{CO})'_\infty}{A} (e^{-At} - 1) \quad (30)$$

In the next section, eqs. (14), (15), (18), (20), (22)-(24), (26), and (29) will be applied to data for the autoxidation of PEG ($\bar{M}_n = 25,000$) and PPG ($\bar{M}_n = 10^6$) in o-dichlorobenzene at 94° and 85°C, respectively. The results will be tabulated and compared.

III. Results

In Figs. 1 and 3 are shown plots of Eqs. (14) and (15) [values of $[HP]_\infty^{1/2} = 0.45$ and 0.20 were used for PEG and PPG, respectively]. From the linear relationships obtained, average values of k_i of $4.4 \times 10^{-4} \text{ sec}^{-1}$ and $7.5 \times 10^{-4} \text{ sec}^{-1}$ were obtained from Eqs. (14) and (15) for PEG and PPG, respectively. A good linear plot would be anticipated at the higher reaction

times ($R'_i \gg R_i$), cf. plot of Eq. (14), Figs. 1 and 3. Using the following values¹⁴ for PEG at the higher reaction times: $[RH] = 4.2$, $k_p = 3$, and $k_t = 10^6$, the intercept from the plot of Eq. (15) affords a value from which a value of $k_i = 1 \times 10^{-4} \text{ sec}^{-1}$ can be calculated. Thus, there appears to be a large discrepancy between the value of k_i obtained from the slopes of the plots of Eqs. (14) and (15) and the value obtained from the intercept of the plot of Eq. (15). This inconsistency may be partially due to the values assumed for $[RH]$, k_p , and k_t and/or to the assumptions made in deriving Eqs. (14) and (15). A similar inconsistency was observed for PPG.

In Figs. 2 and 4 are shown plots of Eqs. (23a), (24a), and (25a). From plots of these respective equations, average values of A of $1.40 \times 10^{-4} \text{ sec}^{-1}$ and $2.62 \times 10^{-4} \text{ sec}^{-1}$ were obtained for PEG and PPG respectively. From the value of the intercepts obtained from the plots of Eq. (24a) and from the values of A obtained from their slopes, values of $[HP]_\infty = 0.20$ and 0.041 were calculated for PEG and PPG, respectively. (obsd., 0.20 and 0.040). Thus, values obtained from the slopes and intercepts of plots are in better agreement using the more general scheme (Sec. 11b) than the simpler scheme (Sec. 11a).

From known values of k_i and $[HP]_\infty$, Eq. (18) may be written for PEG and PPG, respectively, as

$$\Delta[O_2] = 1.76 \times 10^{-4} t + 1.20 (e^{-2.2 \times 10^{-4} t} - 1) - 0.20 (e^{-4.4 \times 10^{-4} t} - 1) \quad (18a)$$

$$\Delta[O_2] = 0.60 \times 10^{-4} t + 0.24 (e^{-3.75 \times 10^{-4} t} - 1) - 0.040 (e^{-7.5 \times 10^{-4} t} - 1) \quad (18b)$$

Corresponding expressions were obtained from Eq. (29) (from the general scheme)

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by utilizing known values of R_1 , A , $[HP]_0$, and a particular value of $\Delta[O_2]$ at a certain reaction time, e.g., $\Delta[O_2] = 0.20$ at $t = 0.6 \times 10^{-4}$ sec. for PEG and $\Delta[O_2] = 0.028$ at $t = 0.3 \times 10^{-4}$ sec for PPG. From these values of $k_5 = 4.8 \times 10^{-4} \text{ sec}^{-1}$ and $7.1 \times 10^{-4} \text{ sec}^{-1}$ were estimated for PEG and PPG, respectively, [cf. the corresponding values of $k_1 \approx 4.4 \times 10^{-4} \text{ sec}^{-1}$ and $7.5 \times 10^{-4} \text{ sec}^{-1}$ obtained from Eqs. (14) and (15)] for PEG and PPG, respectively. Equation (29) may now be written for PEG and PPG, respectively, as

$$\Delta[O_2] = 0.98 \times 10^{-4} t + 0.69 (e^{-1.4 \times 10^{-4} t} - 1) \quad (29a)$$

and,
$$\Delta[O_2] = 0.29 \times 10^{-4} t + 0.11 (e^{-2.6 \times 10^{-4} t} - 1) \quad (29b)$$

Table 1 contains calculated [Eqs. (18a), (18b), (29a), (29b)] and observed values of $\Delta[O_2]$ at various reaction times for PEG and PPG.

Table 1

Calculated and Observed Values of
 $\Delta[O_2]$ for PEG and PPG

	$\Delta[O_2]$, mole/l.		
Time $\times 10^{-4}$, sec.	----- Calculated -----		Observed
	Eq. (18a)	Eq. (29a)	
PEG			
0.30	0.10	0.07	0.11
0.45	0.16	0.13	0.16
0.60	0.35	(0.20)	0.20
0.75	0.54	0.29	0.25
0.90	0.75	0.39	0.29
PPG			
	<u>Eq. (18b)</u>	<u>Eq. (29b)</u>	
0.15	0.014	0.0085	0.015
0.30	0.055	(0.028)	0.028
0.45	0.11	0.056	0.040
0.60	0.18	0.090	0.050

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Prior to using Eq. (20) to estimate values of $\Delta[> c = 0]$ for PEG, it is first necessary to obtain the value of $(\rho_{CO})_{\infty}$. By employing a value of $(\rho_{CO})_{\infty} = 0.22 \times 10^{-4}$, a plot of Eq. (20') afforded an approximate linear relationship which overlapped the plot for Eq. (14), as would be anticipated, cf. Fig. 1. Similar considerations apply when $(\rho_{CO})_{\infty} = 0.60 \times 10^{-5}$ was used for PPG, cf. Fig. 3. Equation (20) now becomes for PEG and PPG, respectively,

$$\begin{aligned} \Delta[> c = 0] &= 0.22 \times 10^{-4} t + 0.20 (e^{-2.2 \times 10^{-4} t} - 1) \\ &\quad - 0.05 (e^{-4.4 \times 10^{-4} t} - 1) \end{aligned} \quad (20a)$$

and,

$$\begin{aligned} \Delta[> c = 0] &= 0.60 \times 10^{-5} t + 0.032 (e^{-3.75 \times 10^{-4} t} - 1) \\ &\quad - 0.008 (e^{-7.5 \times 10^{-4} t} - 1) \end{aligned} \quad (20b)$$

The corresponding expressions for $\Delta[> c = 0]$ from the general scheme may be similarly obtained as follows: if we utilize a value of $(\rho_{CO})'_{\infty} = 0.22 \times 10^{-4}$ in Eq. (25a), a plot of this equation (cf. Fig. 2) also gives a plot which overlaps that from Eq. (23a), as would be expected. From this value of $(\rho_{CO})'_{\infty}$, Eq. (26) becomes for PEG,

$$\Delta[> c = 0] = 0.22 \times 10^{-4} t + 0.155 (e^{-1.4 \times 10^{-4} t} - 1) \quad (26a)$$

Similarly, when a value of $(\rho_{CO})'_{\infty} = 0.60 \times 10^{-5}$ is used in Eq. (25a), a plot of this equation (cf. Fig. 4) also gives a plot which overlaps that from Eq. (23a). Equation (26) becomes for PPG,

$$\Delta[> c = 0] = 0.60 \times 10^{-5} t + 0.023 (e^{-2.62 \times 10^{-4} t} - 1) \quad (26b)$$

Table 2 summarizes calculated [from Eqs. (20a), (20b), (26a), and (26b)] and observed values of $\Delta[\gamma c = o]$ at various reaction times for PEG and PPG, respectively.

Table 2
Calculated and Observed Values of
 $\Delta[\gamma c = o]$ for PEG and PPG

	<u>$\Delta[c = o]$, mole/l.</u>		
<u>Time $\times 10^{-4}$, sec.</u>	<u>----- Calculated -----</u>		<u>Observed</u>
	<u>Eq. (20a)</u>	<u>Eq. (26a)</u>	
	<u>PEG</u>		
0.30	0.01	0.014	0.019
0.60	0.032	0.044	0.055
0.90	0.074	0.088	0.10
1.2	0.13	0.14	0.15
	<u>PPG</u>		
	<u>Eq. (20b)</u>	<u>Eq. (26b)</u>	
0.15	0.0007	0.0014	0.002
0.30	0.004	0.0054	0.0077
0.60	0.016	0.018	0.020
0.90	0.034	0.033	0.034

Prior to using Eq. (22) to estimate values of $\Delta\eta$, a value of f_1 must be obtained. From data provided¹⁴ a value of $f_1 = 60$ was estimated for PEG. Then Eq. (22) becomes for PEG (sufficient data was not available for a similar treatment for PPG),

$$\Delta\eta = 13.2 \times 10^{-4} t + 12 (e^{-2.2 \times 10^{-4} t} - 1) - 3 (e^{-4.4 \times 10^{-4} t} - 1) \quad (22a)$$

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Prior to using Eq. (20) to estimate values of $\Delta[> c = 0]$ for PEG, it is first necessary to obtain the value of $(p_{CO})_{\infty}$. By employing a value of $(p_{CO})_{\infty} = 0.22 \times 10^{-4}$, a plot of Eq. (20') afforded an approximate linear relationship which overlapped the plot for Eq. (14), as would be anticipated, cf. Fig. 1. Similar considerations apply when $(p_{CO})_{\infty} = 0.60 \times 10^{-5}$ was used for PPG, cf. Fig. 3. Equation (20) now becomes for PEG and PPG, respectively,

$$\begin{aligned} \Delta[> c = 0] &= 0.22 \times 10^{-4} t + 0.20 (e^{-2.2 \times 10^{-4} t} - 1) \\ &\quad - 0.05 (e^{-4.4 \times 10^{-4} t} - 1) \end{aligned} \quad (20a)$$

and,

$$\begin{aligned} \Delta[> c = 0] &= 0.60 \times 10^{-5} t + 0.032 (e^{-3.75 \times 10^{-4} t} - 1) \\ &\quad - 0.008 (e^{-7.5 \times 10^{-4} t} - 1) \end{aligned} \quad (20b)$$

The corresponding expressions for $\Delta[> c = 0]$ from the general scheme may be similarly obtained as follows: if we utilize a value of $(p_{CO})'_{\infty} = 0.22 \times 10^{-4}$ in Eq. (25a), a plot of this equation (cf. Fig. 2) also gives a plot which overlaps that from Eq. (23a), as would be expected. From this value of $(p_{CO})'_{\infty}$, Eq. (26) becomes for PEG,

$$\Delta[> c = 0] = 0.22 \times 10^{-4} t + 0.155 (e^{-1.4 \times 10^{-4} t} - 1) \quad (26a)$$

Similarly, when a value of $(p_{CO})'_{\infty} = 0.60 \times 10^{-5}$ is used in Eq. (25a), a plot of this equation (cf. Fig. 4) also gives a plot which overlaps that from Eq. (23a). Equation (26) becomes for PPG,

$$\Delta[> c = 0] = 0.60 \times 10^{-5} t + 0.023 (e^{-2.62 \times 10^{-4} t} - 1) \quad (26b)$$

decomposition ($k_1 = 4.4 \times 10^{-4} \text{ sec}^{-1}$ and $k_5 = 4.8 \times 10^{-4} \text{ sec}^{-1}$) which are in good agreement. Chien and Boss¹⁷ have indicated a value of about $1 \times 10^{-4} \text{ sec}^{-1}$ for the rate constant for polypropylene hydroperoxide decomposition at 95°C . The values of $(\rho_{\text{CO}})_\infty$ are similar for both schemes. At relatively large reaction times, there are large discrepancies between values obtained for $\Delta[\text{O}_2]$ from both schemes. This behavior may be due to the formation of oxidation products at the high reaction times which inhibit the oxidation rate. This is postulated in view of the fact that the oxidation rates of polyolefins¹⁷ generally increase more rapidly than observed for PEG.

It may also be mentioned that when intramolecular propagation was included in the simple scheme, greater discrepancies between calculated and observed values of reaction variables resulted than when it was neglected. As previously indicated, after initial reaction times, chain scission occurs to a great extent thereby lessening the number of hydrogens per polymer molecule available for intramolecular propagation.

Despite the somewhat better agreement provided by the more general scheme between calculated and observed reaction variables, it is difficult to account for the change in mechanism that apparently results after initial autoxidation (very low conversion) times, i.e., termination by recombination of polymeric peroxy radicals no longer occurs after initial reaction times. In view of this and discrepancies between calculated and observed values at relatively low (at relatively low reaction times, discrepancies would be expected for the simple scheme) and high reaction times, more work on PEG autoxidation is indicated before any final decision can be reached as to which scheme is the more preferable.

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Acknowledgment

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Fig. 1. Plots of Eqs. (14), (15), and (20') for the autoxidation of PEG;

○ ----- Eq. (14.); Δ ----- Eq. (15.); □ Eq. (20').

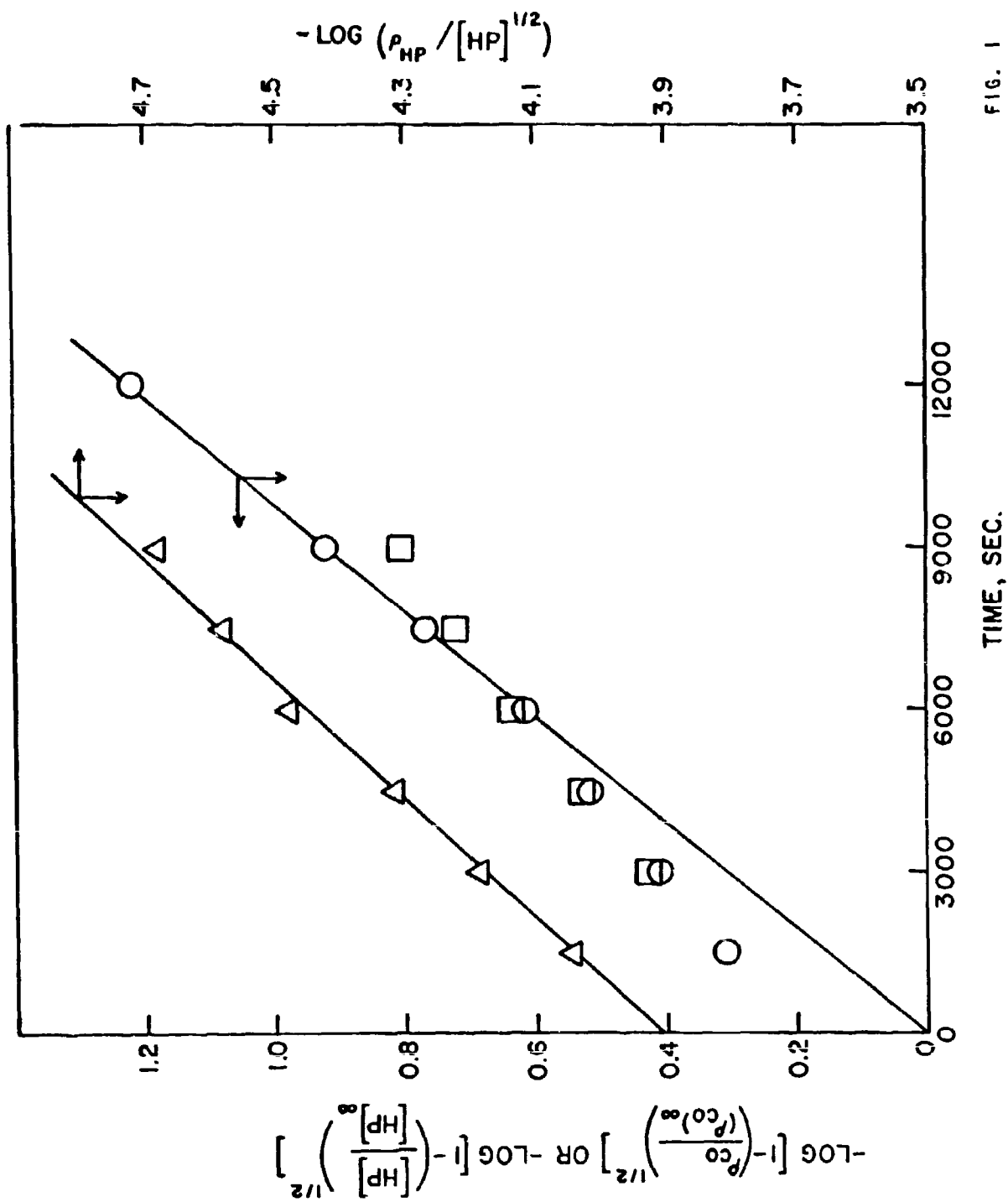


FIG. 1

Fig. 2. Plots of Eqs. (23.a), (24.a), and (25.a) for the autoxidation of PEG;

○----- Eq. (23.a.); Δ----- Eq. (24.a.); □----- Eq. (25.a.).

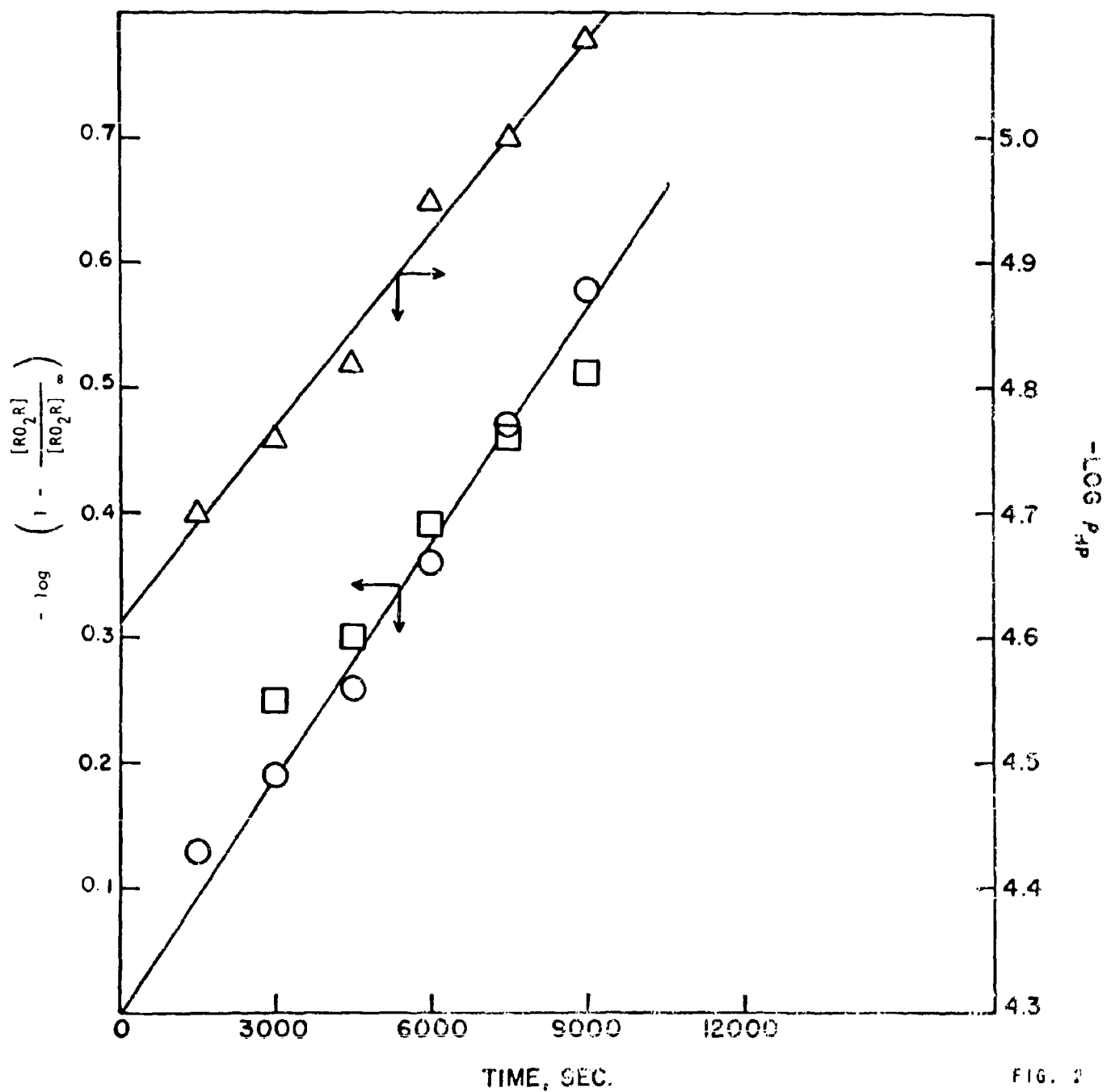


FIG. 2

Fig. 3. Plots of Eqs. (14), (15), and (20') for the autoxidation of PPG;

○----- Eq. (14); Δ----- Eq. (15); □----- Eq. (20').

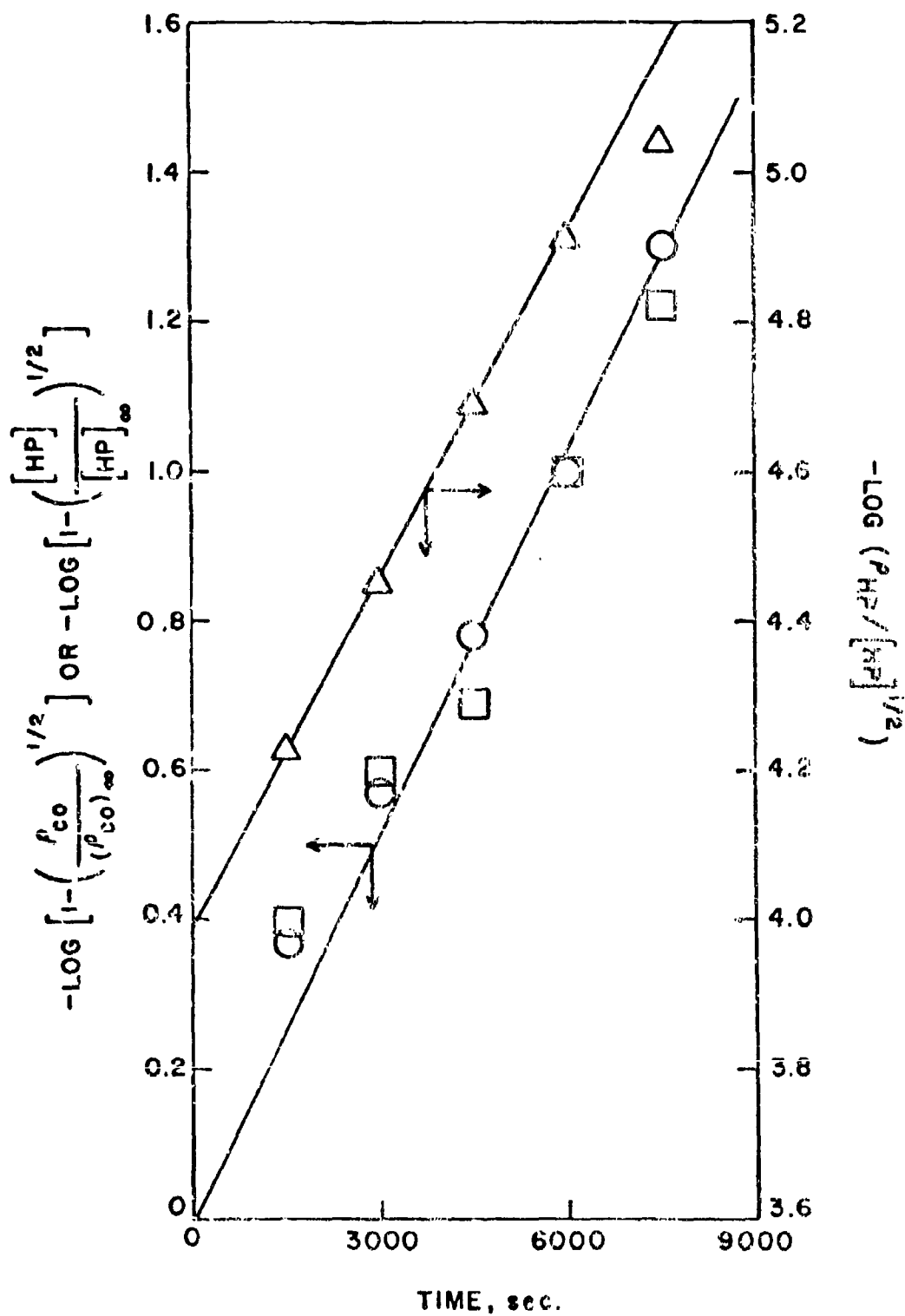


FIG. 3

Fig. 4. Plots of Eqs. (23.a), (24.a), and 25.a) for the autoxidation of PPG;

○ ----- Eq. (23.a); Δ ----- Eq. (24.a); □ ----- Eq. (25.a).

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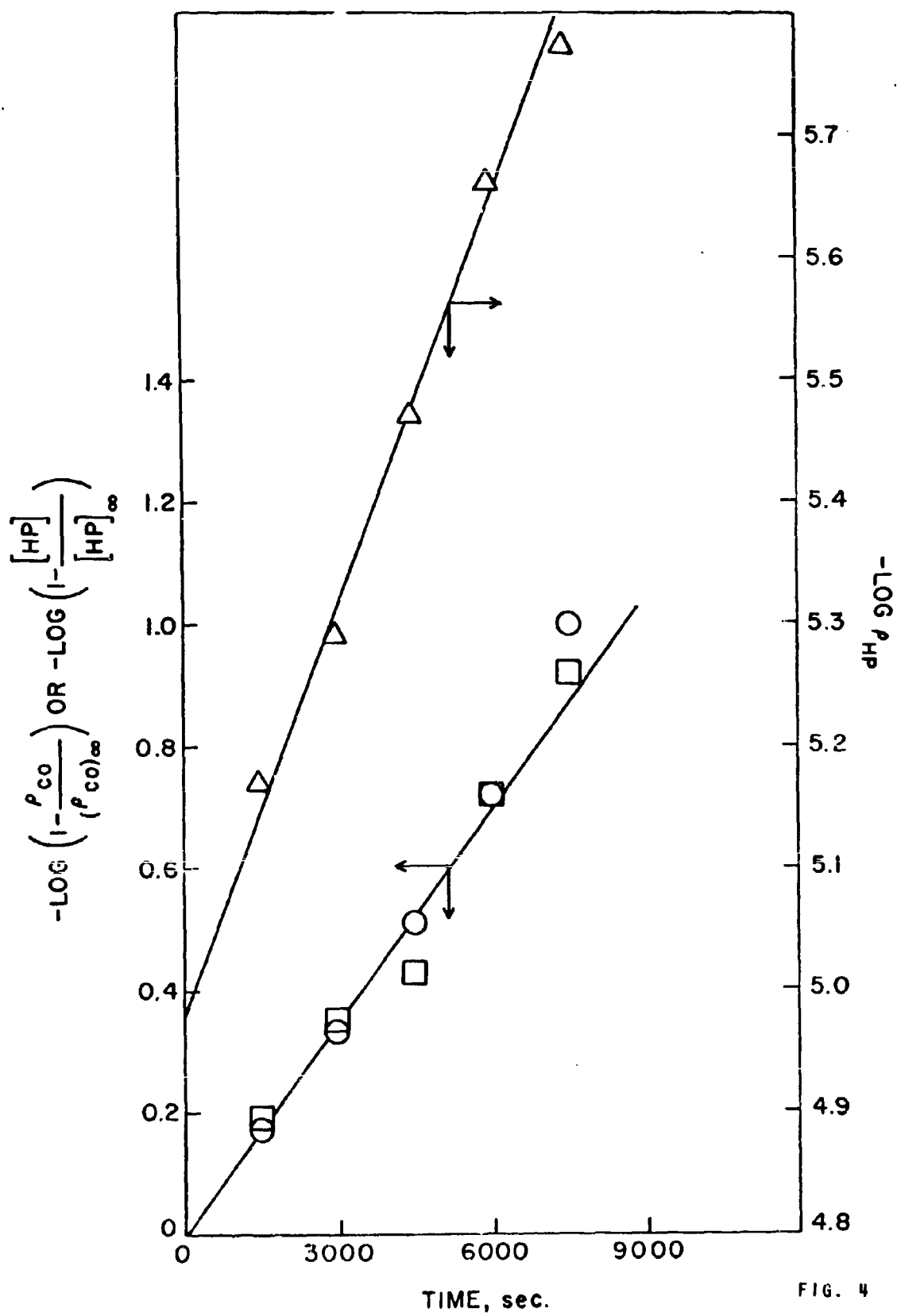


FIG. 4

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13. ABSTRACT Data reported for the autoxidation of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) in solution at relatively long reaction times were analyzed. A relatively simple and a more general kinetic scheme with corresponding rate expressions were used. It was found that the more general scheme gave somewhat more satisfactory agreement between calculated and observed values of several reaction variables. Limitations in the applications of both schemes to PEG and PPG autoxidations are mentioned.			

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